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From Light to Heavy: Addressing Gaps in Rare Earth Element Extraction at the Lynas Advanced Materials Plant

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ABSTRACT

The Lynas Advanced Materials Plant (LAMP) in Kuantan, Malaysia, exemplifies sustainable practices in rare earth element (REE) separation processes through its efficient solvent extraction techniques using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (HEH/EHP or P507) and di-2ethylhexyl-phosporic acid (D2EHPA or P204) to separate REEs from monazite ore sourced from Mt. Weld, Australia. LAMP achieves a remarkable 99% yield for light REE separation in areas such as lanthanum, cerium, praseodymium, and neodymium. It faces challenges separating heavy REEs due to the low content in its concentration to be cost-effective. This limitation underscores the need for improved solvents or alternative methods like ion exchange to enhance heavy REE recovery, particularly yttrium, gadolinium, terbium, and dysprosium, which is of interest to Malaysia to separate its non-radioactive heavy REE from ion-adsorbed clay. Insights from LAMP's processes offer valuable lessons in developing robust REE separation strategies that align with global demand, green technology, and environmental and social impact.

Keywords: REE; solvent extraction; Lynas; ion-adsorbed clay

1. Introduction

Rare earth elements (REE), or rare earth metals or minerals, are seventeen chemical elements in the periodic table. The elements are the fifteen lanthanides – lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) atomic numbers 57 to 71 - and yttrium (Y) and scandium (Sc) atomic numbers 39 and 21 respectively. Y and Sc are grouped together with the lanthanides due to their similarity in chemical properties. In discussing REE separation, we categorise the REEs into three: light REE (LREE), medium REE (MREE), and heavy REE (HREEs) [1]. The LREEs are the elements La, Ce, Pr, and Nd. The MREE are Sm, Eu, and Gd, and the HREE are Tb to Lu, including Y and Sc. Despite being termed as rare elements, some of these elements are relatively abundant in the earth's crust [2].

REEs are important and critical minerals due to their high-value contribution to various technological applications and their limited availability [3]. REEs are used in renewable energy technologies like wind turbines and electric car batteries, defence applications like missiles and radar systems, and catalysts for clean energy production. and producing medical imaging equipment and electronic devices such as smartphones and computers [3]. Their effectiveness in various technologies depends on their purity and specific composition. For example, neodymium is a key component in producing high-power magnets in electric vehicles and wind turbines [4]. However, its effectiveness relies on being separated from other REEs to ensure the required magnetic properties. Similarly, dysprosium enhances the heat resistance of neodymium magnets but must be effectively separated to achieve this [5]. Efficiently separating REE enables manufacturers to produce advanced materials with tailored characteristics essential for cutting-edge technologies [6]

REE-bearing ores are found in various geological environments. They can be found in mineral deposits, including igneous rocks, hydrothermal veins, and certain sedimentary rocks. These elements can also be found in seabed deposits and deep-sea muds [7]. Monazite, bastnäsite, xenotime, and ionic adsorbed clays are all soil types that contain REEs. These soils are important sources of REE and are often mined for their content. Monazite is a phosphate mineral that contains thorium (Th), Ce, La, Nd, and other light REE (LREE). It is often found in beach sands and heavy mineral deposits. Bastnäsite is a carbonate mineral that contains Ce, La, Nd, and other REE. It is primarily mined in China and the United States. Xenotime is a rare-earth phosphate mineral that contains Y and other REEs. It is typically found in pegmatites or in association with granitic intrusions. Ion-adsorbed clay (IAC) refers to soils containing HREE, such as Gd, Tb and Y, within their structure. They can be found in weathered granitic rocks [8]. In Malaysia, IAC is found along the Asian tin granitic belt. It consists mainly of LREE and HREE, including Y and Sc [9-10]. Thus, there is interest in extracting and separating these valuable minerals. The method of separation of these REEs is solvent extraction as per Lynas Advance Material Plant (LAMP). This study will review the separation process at LAMP, identify gaps in the separation of Malaysian IAC REE, and propose an alternative solution.

2. Findings

Malaysia reportedly has 16.1 metric tonnes of this resource worth RM809.6 billion and has strategised to exploit the resource laid out in the *Pelan Hala Tuju Teknologi Bahan Termaju Nasional* (Advanced Materials) 2021-2030 [11]. Studies show the concentration and composition of the REEs differ between those found in the western belt, the eastern belt, the north side, and the south side of the Asia tin range [12]. They are considered significant in quantity when more than 500 ppm in concentration [13]. The REE levels and compositions are found to vary in different geological formations. From studies of REE versus petrography, weathered granite with iron nodes with >500 ppm REE. Laterite areas with bauxite have a low REE level and a high Al_2O_4 and K_2O content. Pyroclastic soils with 200 to 400 ppm REE [14]. Even though the REE content is not significant in pyroclastic soils, they are found with significant Sc, such as in Paloh, Gua Musang, Kelantan. In a vertical soil layer evaluation, the researcher found 27% Sc in 63 ppm REE in the top soi, 6% Sc in 132 ppm REE in the middle layer, and 3% Sc in 161 ppm REE in the bottom layer (above the rock formation). Scandium at 2 to 5 ppm is considered good to be developed [15].

LAMP's processes consist of RE Concentrate from monazite ore sourced from Mt. Weld, Western Australia, Cracking and Leaching, Solvent Extraction for REE separation, and REE product finishing Fig. 1 [16]. LAMP currently produces 22,000 MT/year of REE products, including PrNd oxides. LAMP uses concentrated sulfuric acid (H2SO4) in the cracking plant to crack the REE concentrate phosphate into sulphates at high temperatures in rotary kilns. The REE sulphate is then water leached, and the REE is dissolved as REE sulphate solution. pH is adjusted with magnesium oxide (MgO). The liquor is fed into the REE separation plant. Undissolved solids containing thorium (Th) and uranium (U) are transferred to a residue storage facility. REE separation is achieved through continuous counter-current mixer settler solvent extraction. In this area, solvents mono-2-ethylhexyl ester (P507), di(2-ethylhexyl)phosphoric acid, 2-ethylhexylphosphonic acid (P204), and tertiary amines are used as extractants. Sulfonated Kerosene and Isopropyl Alcohol are used as additives for the solvents. High caustic solution (NaOH) concentrations are used in the saponification section, and high concentrations of H2SO4 and hydrochloric acid (HCl) are used in the stripping sections.

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This process achieves a 99% yield for light REE separation in areas such as lanthanum, cerium, praseodymium, and neodymium. in its concentrate to be cost-effective [17].

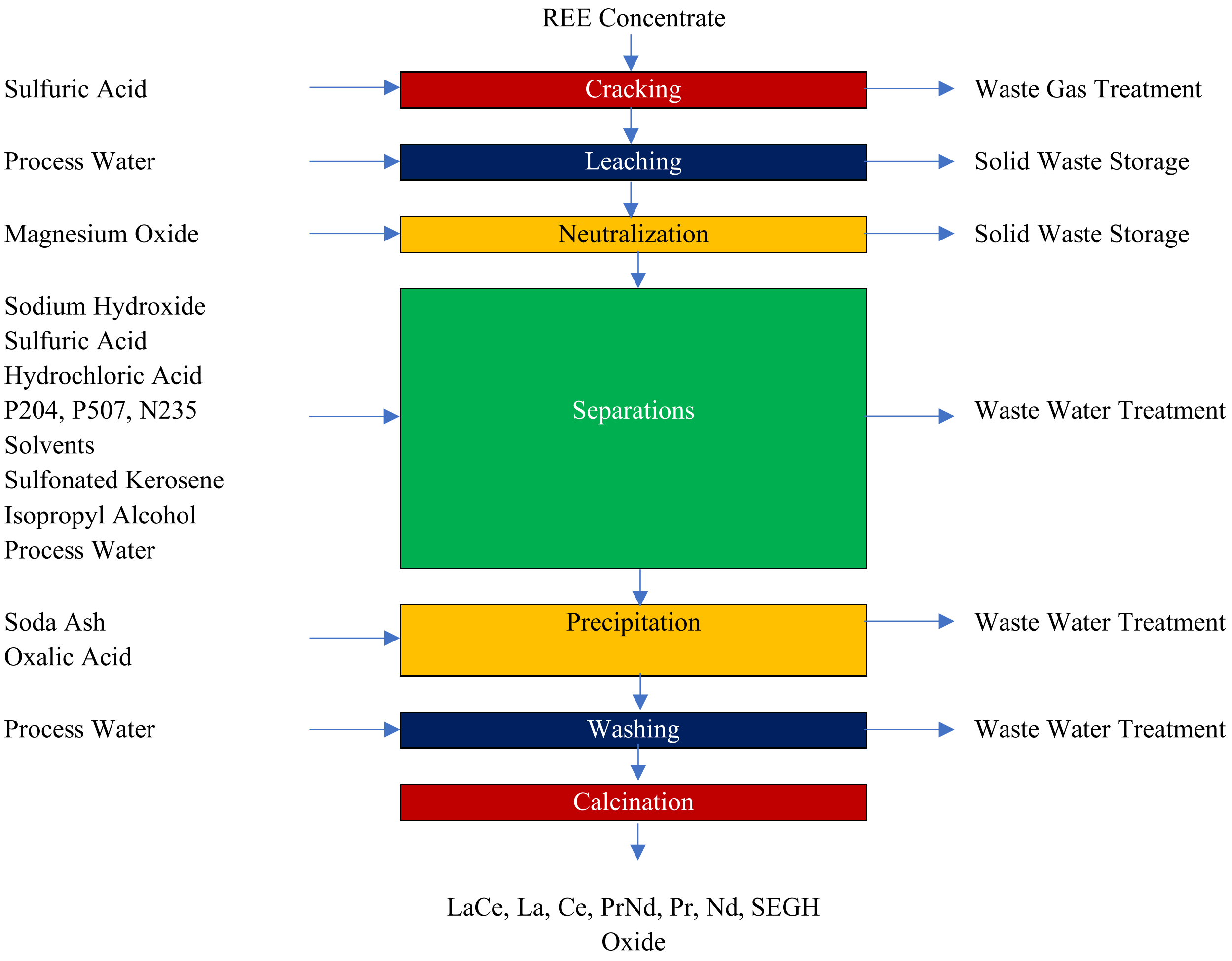

Fig. 1: Simplified LAMP Process Flowsheet

Due to their low content, separating heavy REEs is challenging. Thus, MREE and HREE are not separated but kept as a single SEGH product. LAMP will produce Tb dan Dy by 2025 [18]. LAMP does not separate Y or Sc as it is not in its feed composition. These two facts leave Malaysia with an unanswered question about how to separate Y, Sc, and the other HREE that are significant in quantities for REE in ion-adsorbed clay [19].

On another note, LAMP faces a challenging situation when their REE concentrate contains naturally occurring radioactive material (NORM) with 1600 ppm thorium and 29 ppm uranium typical of monazites. The Th and U end up as the Water Leach Purification (WLP) from the water leaching process. These radioactive materials are typical in monazite, similar to REE from tin mining. LAMP radioactive concentration values were higher in WLP than the lanthanide concentrate, at 232 ppm Th (7.2 Bq/g), compared to the natural background of Malaysian soil. Regulatory control is Th concentration below 1Bq/g [20].

3. Discussion

Malaysia found REE in weathered granite rocks as ion-absorbed clay, as non-radioactive REE (NR-REE) as opposed to the radioactive REE from a monazite rare earth body as Lynas. REE in ionic clay has been identified as a potential source, abundant and unexplored, mainly in the states of Terengganu and Kelantan, and holds the promise of being a valuable source of REE. The clay exhibits unique properties with HREE, including Sc and Y, making it an intriguing candidate for sustainable extraction methods [21-23], not just by solvent extraction but also by other methods, such as ion exchange or membrane filters.

The challenge for REE separation of ion-adsorbed clay is the high HREE, Sc, and Y. Separation is possible via solvent extraction at a high extraction rate of >99%. Ion-adsorbed clay REE is reported to have high silica, aluminium, and calcium impurities and smaller amounts of iron, lead, and manganese [24]. These impurities affect the product quality and further REE separation method and cost [25].

The separation method of Tb, Dy, and other high-value REE by solvent extraction offers more research opportunities with new extractants and ligands. Nevertheless, the separation of LREE as LAMP is fundamental for knowledge contribution. Fig. 2 shows Lynas's current flow sheet for LREE and MHEE separation. It follows a binary separation scheme where, in one cascade, an REE feed is separated into two cuts, the raffinate and the extract [26]. The extract is stripped from the extractant using strong acid.

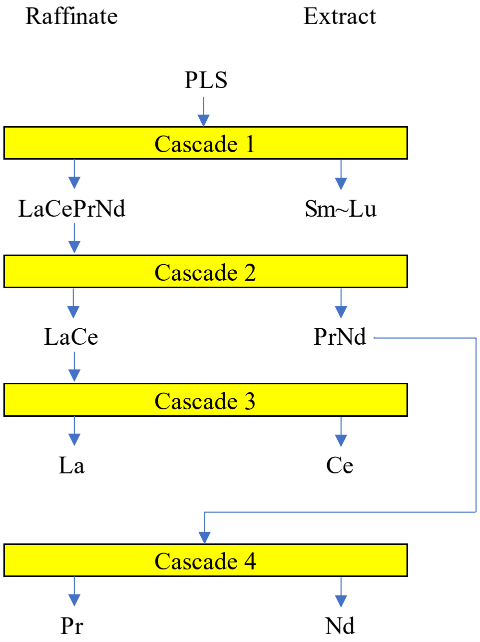

Fig. 2: Simplified flowsheet of Lynas separation circuit

In Fig. 2, the first cascade separates the feed REE along the Nd/Sm line. Sm to Lu are distributed into the extractant while the LREE, La to Nd, remain in the raffinate. Sm to Lu in the extractant is stripped with strong acid. In the second cascade, the LREEs are separated along the Ce/Pr line to obtain LaCe in the raffinate and PrNd in the extract. PrNd in the extractant is stripped with strong acid. In the third cascade, LaCe is separated, with Ce being extracted and La (99.9%) as the raffinate. Ce in the extractant is stripped out with acid as pure Ce (99.9%). In the fourth cascade, Pr/Nd is separated to obtain Pr (99.9%) in the raffinate, and Nd is extracted and stripped with strong acid to become pure Nd (99%).

Fig. 3 shows the flow sheet for HREE separation. Similar to LREE separation, it also follows a binary separation scheme where, in one cascade, an REE feed is separated into two cuts, the raffinate and the extract. The extract is stripped from the extractant using strong acid. SmEuGd is separated from HREE in the first cascade, Cascade 5, along the Gd/Tb line. HREE are distributed into the extractant while the SmEuGd remains in the raffinate. HREE are stripped from the extractant using a strong acid. In the second cascade, Cascade 6, the HREE are separated along the Dy/Ho line to obtain TbDy in the raffinate and Ho to Lu in the extractant. Ho to Lu mix in the extractant is stripped with strong acid. In the third cascade, Cascade 8, Tb/Dy is separated, with Dy being extracted and Tb (99.9%) as the raffinate. Dy in the extractant is stripped out with acid as Dy (99.9%). The complete separation circuit at LAMP is likely like that shown in Fig. 4, with other circuits for removing impurities such as aluminium and zinc.

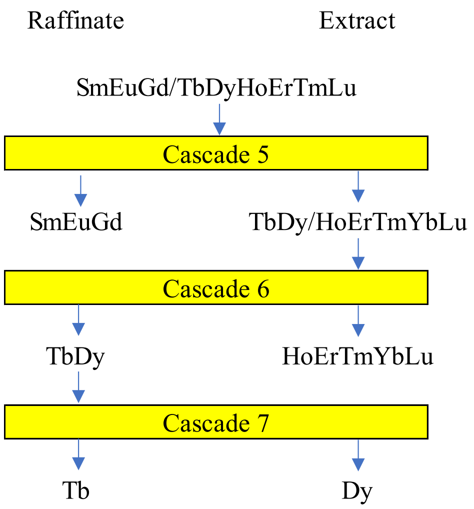

Fig. 3: Simplified flowsheet of Lynas Tb Dy separation circuits

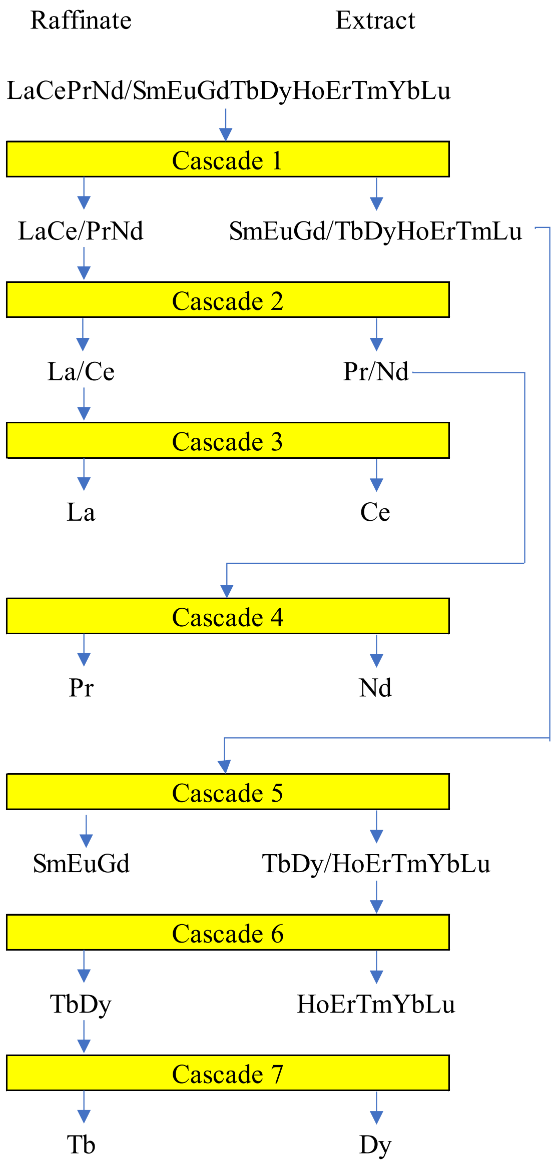

Fig. 4: Simplified flowsheet of Lynas LRE, MRE, HRE Tb Dy circuits

In any ion exchange process, whether liquid-liquid or liquid-solid, the basic principles of the REE ion exchange follow stoichiometry and can be represented by Eq. 1 in liquid-liquid separation and Eq. 2 for liquid-solid separation.

$$3RH^{+}\ (org) + 3Ln^{3+}\ (aq) = 3RLn^{3+}\ (org) + 3H^{+}\ (aq) \tag{1}$$

Where R is the resin, Ln represents a trivalent lanthanide or REE. (org) denotes that it is an organic solvent and (aq) as aqueous.

$$3RH^{+}\ (s) + 3Ln^{3+}\ (aq) = 3RLn^{3+}\ (s) + 3H^{+}\ (aq) \tag{2}$$

Where R is the resin, Ln represents a trivalent lanthanide or REE. (s) denotes that the resin, the extractant, is solid and (aq) is aqueous.

Where solvent extraction is suitable for high concentration and constant feed composition, ion exchange is flexible to low concentration and varying feed composition. Separate batteries are required for each impurity removal in solvent exchange, whilst loading and stripping columns are used in the ion exchange method. REE separation is commonly used in a binary mixer settler system with flammable, high-volatility components in the solvent mix, thus causing a potential danger to the environment. In contrast, ion exchange can separate REE in one go through a column. Large footprint high capital cost and operational cost are required for solvent extraction and the opposite for ion exchange. The conventional method of separating REE by solvent extraction is associated with high operational costs and environmental degradation [27-28]. On the other hand, the ion exchange method has been identified as an environmentally friendly and economically viable alternative [29-31].

Recent developments in solvent extraction are a synergising effect of two solvents [32] to increase the extraction capacity of new solvent extractant [33-34], and ionic liquid [35]. Resins for ion exchange are solvent-impregnated resins (SIRs) [36-39] Other methods are using natural sources of ligand and membrane technology [40].

Either way, the industry should consider REE separation methods for their energy consumption, cost analysis, process efficiency, economic feasibility with proper environmental impact and risk assessment, technology innovation, and other factors [41].

5. Conclusion

Malaysia has REE in ion-adsorbed clay in weathered granitic rocks. For its exploitation, the factor to consider for mining is not the concentration but the value as assessed from its composition. Processing low-quantity REE with high capital and complex operation of mixer-settle solvent extraction units at IAC mining sites is not feasible. Referencing LAMP operation, the missing process is for the extraction of HREE, Sc, and Y. Improved solvent technology and another method of separation need more explicit research and development. The ion exchange method seems viable. This process needs confirmation to be suitable for applying to Malaysian IAC REE.

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